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Project Summary

Modification of Spill Factors Affecting Air Pollution: Volume I. An Evaluation of Cooling as a Vapor Mitigation Procedure for Spilled Volatile Chemicals

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Spilled chemicals that pose a hazard to the land and water ecosystem can also provide a significant vapor hazard. Although the vapors released by such chemicals may ultimately be dispersed in the environment with few long-term effects, they do pose a hazard to life and property downwind of the spill.

Among the vapor amelioration techniques that have been considered is the use of a coolant to lower the temperature of a spill and reduce its equilibrium vapor pressure. This program was conducted as a feasibility study of that mechanism.

Four potential coolants were examined: water ice, dry ice, liquid carbon dioxide, and liquid nitrogen. Further evaluation based on laboratory studies and limited scaled-up tests established dry ice as the most versatile coolant choice. Water ice does not cool sufficiently. Liquid nitrogen and carbon dioxide require large quantities of material and produce a dense obscuring cloud that has some adverse implications. Dry ice avoids these problems and is readily available at a reasonable cost, but some method is required for crushing and distributing the dry ice on the spill. A prototype unit was thus developed consisting of a crusher and a pneumatic conveyor to perform these functions.

A pool of diethyl ether with 2.23 m^2 (250 ft^2) of surface was cooled to -60°C (-76°F) using 408 kg (900 lb) of dry ice fed at a rate of 13.6 kg/min (30 lb/min). A measurable reduction in downwind vapor concentration was realized. Pool temperature was still below -10°C (14°F) 2 hr after dry ice discharge was terminated.

This program has established the feasibility of the mechanism, but additional work is necessary to establish practicality, define materials to which cooling is applicable, and optimize the dispensing equipment.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Many of the chemicals that pose a hazard to the land and water ecosystem when spilled can also provide a significant vapor hazard. Although the vapors

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released by such chemicals may ultimately disperse into the environment with little long term effect, they do pose an immediate hazard to life and property downwind of the spill. In addition, a hazard exists to those responding to the spill who must remain in the area for the duration of the incident.

The vapor hazard from spilled chemicals takes two forms: the release of toxic fumes that pose a life hazard even at low concentrations (parts per million), and the release of flammable vapors where minimum dangerous concentrations are usually above 1%. Some chemicals may exhibit both hazards, but toxicity, with its lower allowable concentration, will be the controlling feature.

The great difference in minimum hazard levels creates two distinct problems. In the case of flammable vapors, small increments of reduction can be meaningful. For toxic materials, the ability to provide meaningful mitigation of the hazard may lie only with reduction of the equilibrium vapor pressure.

A number of vapor amelioration techniques have received consideration. A review of the techniques conducted under U.S. Coast Guard sponsorship shows that most are ineffective. The techniques of mechanical covers, induced air movement, vapor scrubbing, and vapor phase reaction are in this category. The techniques of foam blanketing and liquid phase modification are the only ones that in their present state of development have had any practical demonstration and can pass the criteria of cost, availability, deployment, and application. The degree of vapor control that can be achieved with these two techniques is beneficial where flammable vapors are the hazard. But where the vapor hazard is one of toxicity and hazardous vapor concentrations are in the parts per million range, such techniques are not adequate.

Maintenance of vapor levels in the parts-per-million range appears to require a mechanism to reduce the equilibrium vapor pressure. One potential mechanism of vapor control may achieve that end: the use of a coolant. Reducing the temperature of the spill reduces the equilibrium vapor pressure and the rate of vapor release per unit of time.

This technique has been addressed in two programs, but no systematic investigation has been conducted. Based on these studies, EPA inaugurated a detailed program to evaluate the potential of cooling and, if warranted, to conduct a simulated spill scenario to define feasibility.

Discussion of Results

This study establishes the basic feasibility of the cooling concept. A literature search and data evaluation delineated an extensive list of potential coolants. Practical considerations of cost, availability, safety, and field handling reduced the candidate list to four materials: wet ice (solid water), dry ice (solid CO_2), liquid CO_2, and liquid nitrogen.

All four materials are readily available from many sources on short notice and at a reasonable cost. The liquefied gases, N_2 and CO_2, can achieve significant reductions in the temperature of the spill, but they are attended by certain disadvantages. These gases require continuous application, and the effect does not persist if application is discontinued. The boiling of the liquid exaggerates the vapor release from the spilled material, negating some of the benefits of cooling. Both materials produce a dense obscuring cloud above the spill surface. This cloud provides a nonflammable atmosphere, but it is also nonbreathable.

Liquid CO_2 can be released to form solid CO_2, identified as CO_2 snow. But conversion is only 15 percent with current technology, an obscuring cloud is still generated.

Wet ice has certain advantages, but its capability is limited to 0°C (32°F). Ice can react with some materials and will cause a volume increase because of its nonvolatility.

Dry ice, crushed and applied as a particulate, initially showed the best potential for effective, persistent cooling with small material losses and minimal cloud formation. Further evaluation supported by laboratory studies and limited scaled-up tests were able to establish dry ice as the best coolant choice. The bases for this selection are detailed in Table 1. The main comparison was the difference of the temperatures achieved and the rate of rise after coolant application was stopped. A comparison using ethyl ether is shown in Figure 1.

Results

The laboratory results were encouraging, but they were not sophisticated enough to establish the feasibility for field use. Field application necessitated a mechanism to convert the standard form of dry ice blocks (10 x 10 x 1 in.; 25 x 25 x 2.5 cm) to a particulate form and a means for dispensing the particulates to the spill surface. A review of commercial equipment revealed several types of applicable equipment. After a limited testing program, a commercial shredder/crusher was selected. The shredder operation was modified in terms of the speed of rotation and the configuration of the tines to achieve a reasonable yield of particles within an acceptable size range. The distribution covered fine particulates to coarse material of 0.635 to 1.27 cm (1/4 to 1/2 in.). Because of the problem of sublimation, a true size range could not be measured. Efficiency in terms of material out versus material in was in the range of 75%.

Several concepts were evaluated for dispensing the crushed dry ice. A snow blower was originally selected, but its operation reduced the effective discharge to 65%. The combination of snow blower/crusher was a poor selection in real time. The discharge distance was not sufficient to allow operation from a restricted location, and the machine was difficult to manipulate around the spill. A change was made to a pneumatic conveyor, which was made up of an auger feeding the particulate into an air stream with forced discharge through a hose.

The combination unit was mounted on a wheeled frame to provide mobility, but the hose discharge allowed an extended discharge pattern from a single location. Some additional material losses were encountered, reducing efficiency to about 50%.

Field tests were conducted using diethyl ether as a spill simulant: 757 L (200 gal) was spilled into a 7.62- by 6.1-m (25- by 20-ft) impoundment. Dry ice was charged at a rate of 13.61 kg/min (30 lb/min) for 30 min with an effective application of 6.80 kg/min (15 lb/min).

The spill temperature was reduced in that time to an averge of -60°C (-76°F), which resulted in a decrease of the equilibrium vapor pressure from 440 to 4.0 mm of Hg. An absolute measure of vapor reduction could not be obtained because of wind effects. The available data show the effective reduction in the vicinity of the spill to be at least 75% of the free spill value. Typical values show a free spill vapor concentration of 10,000 ppm, which was reduced to 180 ppm by the dry ice application.

Conclusions

The results of this program show that dry ice can significantly reduce the

Table 1. Cryogen Comparisons

Cryogen	Advantages	Disadvantages
Liquefied Nitrogen	*1. Cheaper than CO_2 on a per-pound basis* *2. Extremely low temperatures possible*	*1. Vapor losses occur on storage* *2. N_2 cloud significantly reduces visibility and oxygen levels in vicinity of spill* *3. Larger quantities needed to cool spill than with solid CO_2* *4. Not as cost effective as solid CO_2* *5. Hazardous liquid may be entrained by N_2 vapors*
Liquefied Carbon Dioxide	*1. No storage losses* *2. Reasonable temperature reduction of spill*	*1. Higher liquid CO_2 losses occur upon application to the spill* *2. CO_2 cloud significantly reduces visibility and oxygen levels in vicinity of spill* *3. More expensive than solid CO_2 based on the amount actually applied to the spill*
Solid Carbon Dioxide	*1. Better cost advantage than liquid CO_2 or liquefied N_2* *2. Less application loss than with LN_2 or liquid CO_2* *3. Rapid cooling of spill* *4. No problems with CO_2 cloud* *5. Can be projected over distances* *6. Readily available* *7. Safer than liquefied N_2 or liquefied CO_2 to handle*	*1. Storage losses occur* *2. Grinding necessary before application*
Ice	*1. Safest to use* *2. Most readily available* *3. Can be projected*	*1. Temperature of the spill is not reduced sufficiently* *2. Increases the liquid volume of the spill when the ice melts*
Liquefied Nitrogen	*1. Cheaper than CO_2 on per pound basis* *2. Extremely low temperatures possible*	*1. Vapor losses on storage* *2. N_2 cloud significantly reduces visibility and oxygen levels in vicinity of spill* *3. Larger quantities needed to cool spill than solid CO_2* *4. Not as cost effective as solid CO_2* *5. Possible entrainment of hazardous liquid by N_2 vapors*
Liquefied Carbon Dioxide	*1. No storage losses* *2. Reasonable temperature reduction of spill*	*1. Higher liquid CO_2 losses upon application to the spill* *2. CO_2 cloud significantly reduces visibility and oxygen levels in vicinity of spill* *3. More expensive than solid CO_2 on the basis of amount actually applied to the spill*
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Ice	*1. Safest to use* *2. Most readily available* *3. Can be projected*	*1. Temperature of the spill is not reduced sufficiently* *2. Increases the liquid volume of spill when the ice melts*

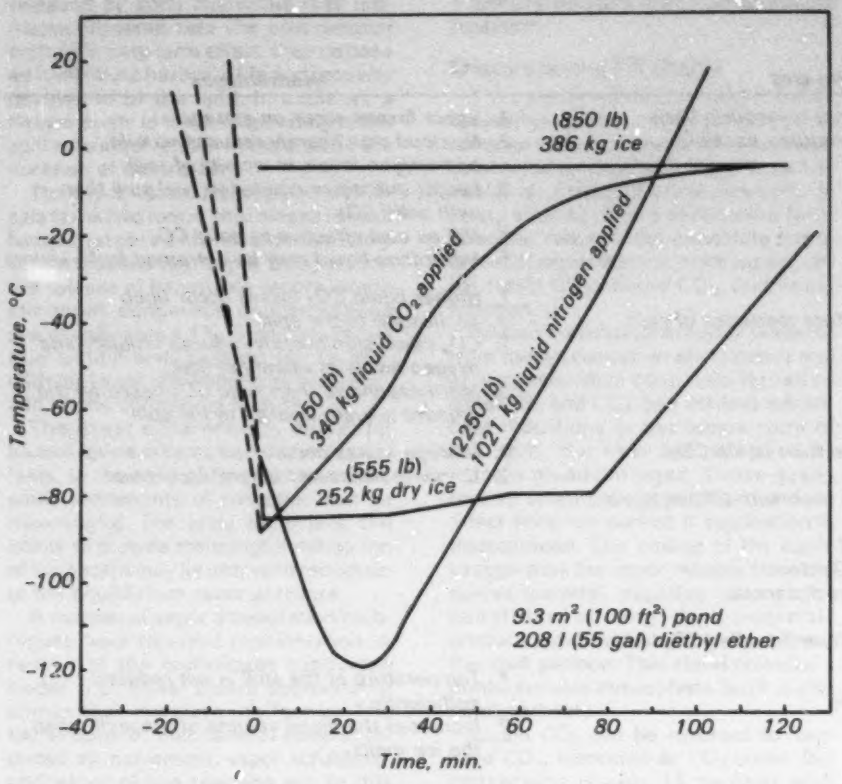

Figure 1. Subscale field test results with ethyl ether—temperature versus time (9.3 m^2 (100-ft^2) pond, 208 L (55 gal) diethyl ether).

temperature of a spilled liquid with a concomitant reduction in the vapor release rate. Crushing the dry ice to an acceptable particulate level and distributing it over the spill surface can be achieved by state-of-the-art techniques.

The equipment evolved in this program required further optimization. Further study must be done on operation, configuration, and materials of construction. The tests that have been conducted are not sufficiently extensive to show clearly a practical, efficient operation in a real-time spill scenario. But they do support continued investigation and evaluation of the cooling concept.

The cooling concept is primarily suited for use with materials that pose a toxic vapor hazard rather than a flammable or explosive vapor hazard. In most cases, aqueous foams provide effective mitigation for such materials.

Foams are a well developed technology in common use by emergency organizations, but they cannot provide the degree of vapor control necessary where toxic levels are in the parts per million range. This study provides a basic guideline for further evaluation of coolants.

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The complete report, entitled "Modification of Spill Factors Affecting Air Pollution: Volume I. An Evaluation of Cooling as a Vapor Mitigation Procedure for Spilled Volatile Chemicals," (Order No. PB 82-108 382; Cost: $9.50, subject to change) will be available only from:
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